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- (54) Title of the Invention: **Coating Method for Particulate Detergent Component**  
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- (22) Filing Date: September 26, 1989
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## **SPECIFICATION**

### **1. Title of the Invention**

Coating Method for Particulate Detergent Component

### **2. Claims**

1. A coating method for a particulate detergent component, characterized in that an aqueous suspension containing water-insoluble or poorly soluble microparticles and a water-soluble film-forming material in a weight ratio of 50:50 to 95:5 is introduced into a flow-type or stirred unit for the particulate detergent component in a coating apparatus; and the particulate detergent component thus coated with the aqueous suspension is dried.

2. A coating method as defined in Claim 1, wherein the particulate detergent component is a single type of particles selected from enzyme particles, bleach particles, bleaching aid particles, fragrance particles, and surfactant particles, or a mixture thereof.

3. A coating method as defined in Claim 1 or 2, wherein the water-insoluble or poorly soluble microparticles have a mean grain size of 0.05–10  $\mu\text{m}$ .

4. A coating method as defined in any of Claims 1–3, wherein the water-insoluble or poorly soluble microparticle are a single type of particles selected from calcium carbonate, titanium dioxide, magnesium carbonate, and zeolite, or a mixture thereof.

5. A coating method as defined in Claim 1–4, wherein the water-soluble film-forming material is a material selected from polyvinyl alcohol, cellulose derivatives, starch derivatives, natural polymer derivatives, polyethylene glycol, and acrylic acid polymers, or a mixture thereof.

6. A coating method as defined in any of Claims 1–5, wherein the coating apparatus is selected from fluid beds, coating pans, fluidized granulators, and stirred granulators.

### 3. Detailed Description of the Invention

#### Field of Industrial Utilization

The present invention relates to a method for manufacturing a coated particulate detergent component that remains stable over time, is only slightly affected by additives, and dissolves readily in water.

#### Prior Art and Problems Thereof

Various detergent additives are commonly used in order to enhance detergency or to obtain added value. Of these, enzymes and bleaches, by their very nature, are easily affected by other detergent additives, and are therefore coated to achieve enhanced temporal stability and to ensure protection from the effects of other additives. Conversely, bleaches and the like sometimes affect the quality of other detergent components, and coating is occasionally performed in order to suppress such effects. Alternatively, coatings are sometimes formed on detergent compositions that have an effect on enzymes or bleaches. Because of these applications, post-coating solubility is an important property of detergent components.

In conventional practice, various methods are used for granule coating. Examples include spray-coating polymer latexes (JP (Kokai) 63-305931) and polymer film-forming materials (JP (Kokai) 50-71583). These methods, however, yield coated products poorly soluble in water, and are thus unsuitable for forming coatings on detergent components. There are also coating methods in which water-soluble, high-melting materials and molten waxes are introduced into stirred granulators (JP (Kokai) 63-32485, 53-6484, etc.). With these methods, coarse grains are formed by particle aggregation, deposits form inside the stirred granulators, the yield is reduced, and other problems are encountered.

#### Means Used to Solve the Aforementioned Problems

As a result of thoroughgoing research aimed at addressing the aforementioned problems, the inventors perfected the present invention upon discovering that a

particulate detergent component that has excellent solubility in water, produces a high yield, forms a minimal amount of coarse grains, and does not adhere to the interior of a granulator during coating can be obtained by a method in which a dispersion obtained by mixing water-insoluble or poorly soluble microparticles and water-soluble film-forming material in a prescribed ratio is introduced into a unit for the particulate detergent component with the aid of a coating apparatus, and the product is then dried to form a continuous film around the particles.

Specifically, the present invention provides a coating method for a particulate detergent component characterized in that an aqueous suspension containing water-insoluble or poorly soluble microparticles and a water-soluble film-forming material in a weight ratio of 50:50 to 95:5 is introduced into a flow-type or stirred unit for the particulate detergent component in a coating apparatus; and the particulate detergent component thus coated with the aqueous suspension is dried.

The coating agent used in the present invention is an aqueous suspension containing water-insoluble or poorly soluble microparticles (referred to hereinbelow as "poorly soluble microparticles") and a water-soluble film-forming material in an appropriate ratio.

The mean grain size of the poorly soluble microparticles should be 0.05–10  $\mu\text{m}$ , and preferably 0.1–5  $\mu\text{m}$ . Examples include calcium carbonate, titanium dioxide, magnesium carbonate, zeolite, clay, kaolin, metal soaps, and macromolecular polymer beads. Various inorganic and organic poorly soluble microparticles can be used. When the poorly soluble microparticles have a mean grain size of less than 0.05  $\mu\text{m}$ , they are difficult to handle because of their low bulk specific gravity, and the aqueous suspension has low fluidity. A mean grain size greater than 10  $\mu\text{m}$  makes it impossible to form a homogenous coating layer on a particulate detergent component.

Examples of suitable water-soluble film-forming materials include polyvinyl alcohol, carboxymethyl cellulose, methylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, starch derivatives, pullulan, shellac, sodium alginate, polyethylene glycol, and acrylic acid polymers. Any other

material may also be used as long as it is readily soluble in water and does not compromise the benefits of the present invention.

The weight ratio of the poorly soluble microparticles and water-soluble film-forming material should be 50:50 to 95:5, and preferably 60:40 to 90:10. It is unsuitable for the water-soluble film-forming material to be contained in an amount greater than the aforementioned ratio because in this case the drying rate of the coating material decreases, and coated particles dissolve in water at a slower pace when added to a detergent. Adding the water-soluble film-forming material in an amount below the aforementioned ratio fails to ensure adequate bonding between the surface of the particulate detergent component and the poorly soluble microparticle or between the poorly soluble microparticles on the surface of the particulate detergent component, yielding an inferior coating layer.

The concentration of the solids in the aqueous suspension can be arbitrarily set anywhere between 1 and 70 wt% in order to adjust viscosity and other physical properties. The solvent may be water or an organic solvent, with water being preferred because of considerations related to the stability and handling of the particulate detergent component.

Colorants (pigments, dyes, and the like), fragrances, and surfactants (the latter are designed to improve the dispersibility of the poorly soluble microparticles) may also be added to the aqueous suspension.

The following devices can be used as the coating apparatus employed in the present invention: (1) fluidized beds such as the Flow Coater manufactured by Okawara Manufacturing, the Aeromatic (fluidized granulation coating drier) manufactured by Fuji Kogyo, and the SPIRA-A-FLOW manufactured by Freund Industrial; (2) coating pans such as the HICOATER manufactured by Freund Industrial and the Doria\*<sup>1</sup> Coater manufactured by Fuji Kogyo; (3) fluidized granulators such as the CF Granulator manufactured by Freund Industrial and the Multiplex Granulator manufactured by Fuji

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<sup>1</sup> Translator's note: Asterisks mark tentative transliterations of proper names that could not be found in the reference materials available to the translator.

Kogyo; and (4) stirred granulators such as the high-speed mixer manufactured by Fukae Kogyo and the particle granulator manufactured by Fuji Sangyo.

No particular restrictions are imposed on the the particulate detergent component used in the present invention. The following examples can be cited.

Examples of enzymes include proteases, esterases, and carbohydrases.

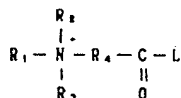
Specific examples of proteases include pepsin, trypsin, chymotrypsin, collagenase, keratinase, esterase, subtilisin, papain, aminopeptidase, and carboxypeptidase.

Specific examples of esterases include gastric lipase, pancreatic lipase, vegetable lipases, phospholipases, coline esterases, and phosphotases.

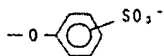
Specific examples of carbohydrases include cellulase, maltase, saccharase, amylase, pectinase, and  $\alpha$ - and  $\beta$ -glycosidase.

Examples of bleaches include sodium percarbonate, sodium perborate, sodium pyrophosphate peroxide, sodium sulfate/hydrogen peroxide adducts, and sodium chloride/hydrogen peroxide adducts.

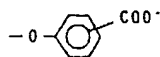
Examples of bleaching aids include tetraacetyl ethylenediamine (TAED), glucose pentaacetate, tetraacetyl glycol urine, sodium alkanoyl oxybenzene sulfonate, and compounds expressed by General Formula (I) below.



(where  $R_1$  is a  $C_1$ - $C_{18}$  alkyl group,  $R_2$  and  $R_3$  are  $C_1$ - $C_2$  alkyl groups,  $R_4$  is  $-(CH_2)_{1-12}-$  and  $L$  is



or



The surfactant may be anionic, cationic, nonionic, or amphoteric. The surfactants described in "Chemistry of Fatty Acids (Shibosan Kagaku)" (by Inaba and Hirano, Koshobo Publishing House, p. 238, 1981) can be cited as specific examples of such surfactants.

Examples of fragrances include isoamyl,  $\alpha$ -pinene,  $\beta$ -pinene, myrcene, terpinolene, limonene, benzaldehyde, methylhexyl ketone, citronellol, linalol, benzyl acetate, linalyl acetate, anethole, citral,  $\ell$ -menthol, and geranyl formate. When a liquid fragrance is used, a porous substance such as dextrin,  $\beta$ -cyclodextrin, or an amorphous silica derivative is impregnated, and granulated particles are coated.

The present invention thus entails coating the surface of a particulate detergent component with a layer composed of poorly soluble microparticles and a water-soluble film-forming material.

According to the present invention, a water-soluble film-forming material is used to bond together the surface of a particulate detergent component and poorly soluble microparticles, and to ensure that bonds form between the poorly soluble microparticles on the surface of the particulate detergent component. In comparison with a conventional coating method (in which a film-forming material alone is used), the proposed coating method allows coating layers to be formed using less film-forming material, minimizes the formation of coarse particles during coating, and reduces the amount of material depositing inside the coating apparatus. Another benefit is that the product dissolves in water more readily when used as a detergent component.

#### Working Examples

The present invention will now be described through working examples, but the present invention is not limited thereby.



The enzyme particles used in Working Examples 1–5 and Comparative Examples 1–5 had grain sizes of 350–1000  $\mu\text{m}$  and were produced by the method described in JP (Kokai) 62-257990. Furthermore, Working Example 6 and Comparative Example 6 entailed using a particulate bleaching aid as the particulate detergent component.

#### Working Example 1

Granulated enzyme (500 g) was introduced into Aeromatic STREA-1 (a fluidized coating apparatus manufactured by Fuji Sangyo), and 60°C air was blown in for fluidization. A coating solution (25 g) consisting of an aqueous suspension comprising 17% calcium carbonate, 3% polyethylene glycol #6000, and 80% water was subsequently sprayed upward for 8 minutes through two bottom-installed fluid nozzles.

The product was then dried for 2 minutes, yielding attractively looking coated granules. The corresponding yield (ratio of particles with a diameter of 350–1000  $\mu\text{m}$ ; same below) was 99.5%, and the coating process was free from the formation of secondary particles, internal equipment deposits, or other types of loss-inducing phenomena. The coated granules had the same water solubility as the uncoated granules. The enzyme did not undergo any discernible coating-induced deactivation.

#### Working Example 2

Granulated enzyme (20 kg) was introduced into FBS-1 (a stirred fluidized bed manufactured by Okawara Manufacturing), and a coating solution (1 kg) consisting of an aqueous suspension comprising 17% calcium carbonate, 3% polyvinyl alcohol, and 80% water was sprayed and applied as a coating through two fluid nozzles provided to the lateral surface of the cylindrical portion of the fluidized bed.

Apart from the fact that the yield was 98.8%, the same results as in Working Example 1 were obtained in terms of water solubility, internal equipment deposits, and the like.

### Working Example 3

Granulated enzyme (20 kg) was introduced into the same apparatus as in Working Example 2, and a coating solution (1 kg) obtained by adding 0.2% of a pigment to an aqueous suspension comprising 17% titanium dioxide, 3% polyethylene glycol #6000, and 80% water was sprayed and applied as a coating.

Apart from the fact that the yield was 98.5%, the same results as in Working Example 1 or 2 were obtained in terms of water solubility, internal equipment deposits, and the like.

### Working Example 4

Granulated enzyme (5 kg) was introduced into the HICOATER manufactured by Freund Industrial, and a coating solution (250 kg) with the same composition as in Working Example 1 was sprayed.

Apart from the fact that the yield was 98.2%, the same results as in Working Example 1, 2, or 3 were obtained in terms of water solubility, internal equipment deposits, and the like.

### Working Example 5

Granulated enzyme (5 kg) was introduced into the same apparatus as in Working Example 4, and a coating solution (250 g) consisting of an aqueous suspension comprising 17% calcium carbonate, 3% hydroxymethylcellulose, 0.08% Poise\* 526 dispersant (sodium polyacrylate), and 80% water was sprayed.

Apart from the fact that the yield was 98.5%, the same results as in Working Example 1, 2, 3, or 4 were obtained in terms of water solubility, internal equipment deposits, and the like.

#### Comparative Example 1

Granulated enzyme was spray-coated with polyethylene glycol #6000 melted at 80°C in the same apparatus and by the same method as in Working Example 1. As a result, spotted particles were obtained, and it was impossible to form a uniform coating layer on the granule surface. In addition, the yield of particles with a diameter of 350–1000 µm was only 92%, and secondary particles were observed forming.

#### Comparative Example 2

A 10% aqueous solution of polyethylene glycol #6000 was spray-coated in the same apparatus and by the same method as in Working Example 1, but a large amount of coarse aggregated particles had formed because the drying rate was low. It was necessary to reduce the spray rate to half the rate of Working Example 1 in order to prevent coarse grains from forming.

#### Comparative Example 3

A 10% aqueous solution of polyvinyl alcohol was spray-coated in the same apparatus and by the same method as in Working Example 1, but the same phenomena as those in Comparative Example 2 were observed. In addition, the resulting coated product had lower water solubility than did the coated product of any of Working Examples 1–5.

#### Comparative Example 4

A 25% aqueous solution of methacrylic acid copolymer was spray-coated in the same apparatus and by the same method as in Comparative Example 1, but the resulting granules had glossy surfaces, and although the yield was high (98.9%), the particles were only minimally soluble in water.

#### Comparative Example 5

Granulated enzyme (5 kg) was introduced into a High Speed Mixer (a stirred granulator manufactured by Fukae Kogyo), the system was heated to 54°C, and molten

80°C polyethylene glycol #6000 was fed under agitation in an amount of 150 g to coat the granulated enzyme.

As a result, a coated material soluble in water was obtained, but coarse granules and precipitates formed in the apparatus, lowering the yield to 88%. In addition, the coated material had a lusterless, rough surface.

The coated materials obtained in Working Examples 1–5 and Comparative Examples 1–5 were evaluated for solubility and storage stability by the methods described below. The results are shown in Table 1.

#### Solubility (Dissolution Rate After 2 Minutes)

A 100 mM Na<sub>2</sub>CO<sub>3</sub> solution (1 L) was introduced into a 1-L beaker, a stirring blade with a blade diameter of 2.5 cm was placed in the center of the beaker at a distance of 2 cm from the bottom, and the system was agitated at 200 rpm. A 0.5-g sample was added under agitation, the agitation was continued for another 2 minutes at a solution temperature of 25°C, and the enzyme activity of the solution was measured by the dinitrosalicylic acid method.

Enzyme activity was measured after 2 and 10 minutes, and the dissolution rate after 2 minutes was calculated using the following formula.

$$\text{Dissolution rate after 2 minutes (\%)} = \frac{\text{Enzyme activity after 2 minutes}}{\text{Enzyme activity after 10 minutes}} \times 100$$

#### Storage Stability (Activity Retention Ratio)

Prescribed amounts of the coated materials obtained in Working Examples 1–5 and Comparative Examples 1–5 were introduced into a powdered laundry detergent and stored for 30 days at a temperature of 30°C and relative humidity of 40–80%. Enzyme activity before and after storage was measured by the dinitrosalicylic acid method, and the activity retention ratio was calculated using the following formula.

$$\text{Activity retention ratio after 30 days (\%)} = \frac{\text{Enzyme activity after storage}}{\text{Enzyme activity before storage}} \times 100$$

**Table 1**

	Coating agent	Yield (%)	Dissolution rate after 2 min (%)	Activity retention ratio (%)
Before coating	—	—	100	80
Working Example 1	Polyethylene glycol #6000/calcium carbonate	99.5	100	96
Working Example 2	Polyvinyl alcohol/calcium carbonate	98.8	100	95
Working Example 3	Polyethylene glycol #6000/titanium dioxide	98.5	98	95
Working Example 4	Polyethylene glycol #6000/calcium carbonate	98.2	99	93
Working Example 5	Hydroxypropylmethylcellulose/calcium carbonate	98.5	100	96
Comparative Example 1	Polyethylene glycol #6000	92.0	100	86
Comparative Example 2	Polyethylene glycol #6000	88.2	98	95
Comparative Example 3	Polyvinyl alcohol	99.5	78	94
Comparative Example 4	Methacrylic acid copolymer	98.9	61	96
Comparative Example 5	Polyethylene glycol #6000	88.0	98	93

#### Working Example 6

TAED (3.5 kg), polyethylene glycol #6000 (1.0 kg), and Glauber's salt (0.5 g) were introduced in a combined amount of 5.0 kg into Lodige mixer M-20 (a mixer manufactured by Matsuzaka Bōeki), and the system was heated for 15 minutes at a jacket temperature of 70°C, a main shaft rotational speed of 200 rpm, and a chamber rotational speed of 1000 rpm. The resulting mixture was extruded and pelletized with a horizontal

extruder/pelletizer (Pelletter Double EXD-60, manufactured by Fuji Paudal; screw diameter: 1.0 mm).

The granules were further processed in a flash mill (FL-200, manufactured by Fuji Paudal) at a rotational speed of 2500 rpm. The processed granules were then sieved, yielding a product with a grain size of 350–1500  $\mu\text{m}$ . A product yield of 86% was achieved.

The granules thus produced were used in an amount of 500 g as a particulate detergent component and coated in the same manner as in Working Example 1. As a result, the yield (as a ratio of particles with grain sizes of 350–1500  $\mu\text{m}$ ) was 99.4%, and the coating process was free from the formation of secondary particles, internal equipment deposits, or other types of loss-inducing phenomena.

#### Comparative Example 6

The same granules (500 g) as those used in Working Example 6 were coated in the same manner as in Comparative Example 1. The resulting yield (350–1500  $\mu\text{m}$ ) was 90.4%, and secondary particles were observed forming during coating.

The coated particles obtained in Working Example 6 and Comparative Example 6 above were evaluated for their dissolution velocity and storage stability on the basis of the criteria described below.

The results are shown in Table 2.

#### Dissolution Velocity (Dissolution Rate After 5 Minutes)

20°C water (150 mL) was introduced into a 200-mL beaker, sodium percarbonate was dissolved to achieve an effective oxygen concentration of 0.05%, a coated material was added to achieve an activator (TAED) purity of 0.04%, the system was agitated for 3 minutes at 100 rpm with the aid of a mechanical stirrer equipped with 2-cm stirring vanes, a 0.3% catalase solution (5 mL) was then added, and the system was agitated for another minute. A 10% potassium iodide solution (10 mL) and a 20% sulfuric acid

solution (10 mL) were added to the resulting solution, and the product was titrated with a 0.1N solution of sodium thiosulfate. Titration was also conducted 10 minutes later by the same method, and the dissolution rate (after 5 minutes) was calculated using the following formula.

$$\text{Dissolution rate after 5 minutes (\%)} = \frac{\text{Titer after 5 minutes (mL)}}{\text{Titer after 10 minutes (mL)}} \times 100$$

#### Storage Stability (Retention Ratio)

Sodium percarbonate and a coated material were mixed (10 g) in a ratio of 1/1 and stored for 2 weeks at 50°C in a 50-mL plastic container. The pre- and post-storage mixing compositions were used to determine the titer of the pre- and post-stored mixtures after 10 minutes by the same titration technique as the one previously used to determine the dissolution velocity, and the retention ratio of the activator (TAED) was calculated using the following formula.

$$\text{Retention ratio (\%)} = \frac{\text{Titer after storage (mL)}}{\text{Titer before storage (mL)}} \times 100$$

**Table 2**

	Coating agent	Yield (%)	Dissolution rate after 5 min (%)	Retention ratio (%)
Before coating	–	–	93.7	84.0
Working Example 6	Polyethylene glycol #6000/calcium carbonate	99.4	92.9	93.1
Comparative Example 6	Polyethylene glycol #6000	90.4	93.5	87.2

## Merits of the Invention

The inventive coating method for a particulate detergent component minimizes the formation of coarse particles resulting from the aggregation of the particulate detergent component during coating and reduces the volume of particles depositing inside the coating apparatus, making it possible to perform a coating operation in which good operability is maintained and particles of the desired grain size are obtained with a high yield. In addition, the improved solubility and storage stability of the resulting high-quality coated particles makes these particles suitable for use as detergent additives.